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(21) International Application Number: PCT/US92/01153 (22) International Filing Date: 12 February 1992 (12.02.92) (30) Priority data: 654,723 12 February 1991 (12.02.91) US 829,494 7 February 1992 (07.02.92) US (71) Applicant: LANDEC LABS, INC. [US/US]; 3603 Haven Avenue, Menlo Park, CA 94025 (US).	(72) Inventors: SCHMITT, Edward, E. ; 2344 Columbia Street, Palo Alto, CA 94306 (US). TSUGITA, Ross ; 657 Smoke Tree Way, Sunnyvale, CA 94086 (US). (74) Agents: REED, Dianne, E. et al.; Morrison & Foerster, 545 Middlefield Road, Suite 200, Menlo Park, CA 94025 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent). Published <i>With international search report.</i>	
(54) Title: TEMPERATURE ZONE SPECIFIC PRESSURE-SENSITIVE ADHESIVE COMPOSITIONS, AND ADHESIVE ASSEMBLIES AND METHODS OF USE ASSOCIATED THEREWITH (57) Abstract Adhesive compositions are provided which are tacky within a predetermined temperature range and will strongly bond an article to a substrate within a given temperature range, but which are substantially nontacky at temperatures outside either range. The adhesive compositions contain a polymeric pressure-sensitive adhesive component and a crystalline polymer which defines the temperature range within which the adhesive composition as a whole is tacky. The invention also provides adhesive assemblies such as adhesive tapes, sheets and the like, as well as methods of use.		

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5 TEMPERATURE ZONE SPECIFIC PRESSURE-SENSITIVE
ADHESIVE COMPOSITIONS, AND ADHESIVE ASSEMBLIES
AND METHODS OF USE ASSOCIATED THEREWITH

Description

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Technical Field

15 The present invention relates to adhesive
compositions, and more particularly, concerns a novel
family of adhesive compositions which are (1) tacky
15 within a predetermined temperature range and (2) will
strongly bond an article to a substrate within a
overlapping but possibly broader temperature range, but
which allows for easy and effortless removal of the
bonded article from the substrate at temperatures outside
20 the range. The novel adhesive compositions are sometimes
referred to herein as "Temperature Zone Specific
Pressure-Sensitive Adhesives", or "TZS-PSAs", and the
combined, overlapping temperature ranges within which the
adhesive compositions are (1) tacky and (2) form strong
25 adhesive bonds is sometimes designated herein as the
"Normal Use Temperature Zone", or "NUTZ".

30 The invention also encompasses adhesive
assemblies such as tapes, sheets, and the like, which are
formulated with these adhesive compositions, as well as
30 methods of using the adhesive compositions in a variety
of contexts.

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Background

Pressure-sensitive adhesives ("PSA") are well-known and are used for a variety of industrial, consumer and medical applications. Pressure-sensitive adhesives are characterized as being normally tacky and exhibiting instant tack when applied to a substrate. A variety of polymers have been used to manufacture PSAs, including acrylic and methacrylic ester homo- or copolymers, butyl rubber-based systems, silicones, urethanes, vinyl esters and amides, olefin copolymer materials, natural or synthetic rubbers, and the like.

Typically, the bond strength of a PSA remains the same or increases with time after application to a substrate. Increased bond strength may result from increased polymer flow or improved wetting over a period of time, or it may result from hydrogen bonding to a polar substrate or from covalent or ionic chemical interactions. Increased bond strength can lead to permanent bonding.

Removal of an adhesive after application to a substrate is often desirable. It need not be gentle removal and, indeed, current products may require a considerable amount of force for removal. In almost all cases, it is most desirable to remove the adhered article from the substrate leaving none of the adhesive on the substrate. For example, tape may be applied to a substrate to mask off a portion during a painting operation, at the completion of which the tape must be removed leaving no residual adhesive. It would be desirable if removal was both complete and gentle. Delicate wallpaper could then be applied with a PSA and removed at a future date. Adhesives applied to human skin, for example on a Bandaid™, wound dressing, transdermal drug delivery device, or monitoring or

stimulating electrodes, having to be removed at a later date could be, without pain or damage. In all of these instances and many others, it may be desirable to be able to readily remove the article and the adhesive gently and completely without damage to the substrate without the need for harsh chemicals or special equipment.

The ideal performance characteristics of an adhesive intended for use on human skin, specifically, present difficult and conflicting technical requirements. The ideal medical adhesive should, first of all, be nonirritating yet bond quickly to skin at the intended site of use. At the same time, clearly, it should not stick to other objects until it is actually applied to the target site. The adhesive should maintain its bond for as long a period of time as necessary and be resistant to inadvertent removal. Furthermore, the adhesive should not be weakened or destroyed by exposure to moisture or high humidity. Finally, in order to provide protection to a wound or to maintain the integrity of placement of an electrode or other device, the adhesive should comply with skin movement and be able to transfer a mechanical load from the adhesive backing to the skin.

The present invention addresses the aforementioned considerations, as it provides adhesive compositions which will strip gently and cleanly from a substrate without leaving a residue or stain, while nevertheless bonding quite strongly to the substrate within a given range of normal use temperatures. These temperature zone specific pressure-sensitive adhesive compositions, or TZS-PSAs, when applied as a thin coating to a surface of a substrate, (1) will exhibit a nontacky adhesive surface for all temperatures below a predetermined range of normal use temperatures, or NUTZ,

(2) will develop tack and attach securely to a substrate at temperatures within the NUTZ, and (3) may be readily and effortlessly removed, when desired, by displacing the temperature of the Tzs-PSA outside the NUTZ. By the term
5 "article" is meant virtually any object, e.g., a bandage, medical device, label, or the like.

Thus, the present invention is based on the discovery that the novel adhesive compositions provided herein can be used to affix an article firmly in place on
10 a substrate with the assurance that the article will remain securely in place for as long as it is needed, within the NUTZ. The invention also enables removal of the article on demand, using a minimum of force and without any destructive effect. Depending on the
15 composition used, removal of a bonded article from a substrate may be effected by heating to a temperature above the NUTZ, or by cooling to a temperature below the NUTZ.

20 Background Art

S.C. Temin, in the Encyclopedia of Polymer Science and Engineering, vol. 13 (New York: John Wiley & Sons, 1988), at pp. 345-368, and the Handbook of Pressure-Sensitive Adhesive Technology, ed. Donatas Satas
25 (New York: Van Nostrand Reinhold Co., Inc., 1982), both provide a comprehensive overview of medical and other adhesives. A.H. Landrock, Adhesives Technology Handbook, (Park Ridge, New Jersey: Noyes Publications, 1985), pp. 154-156, and T. Flanagan, "Hot-Melt Adhesives", in the
30 Handbook of Adhesive Bonding, et. C.V. Cagle (New York: McGraw-Hill, 1982), at pp. 8-1 to 8-17, describe hot-melt adhesives, i.e., adhesives which are applied to a substrate as a melt and which solidify and bond upon cooling.

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U.S. Patent No. 3,284,423 to Knapp describes a pressure-sensitive, cross-linked adhesive copolymer which is claimed to be storage stable in solution but readily cured when coated and heated. The copolymer consists of
5 acrylic acid esters, lower alkyl acrylates (1-8 carbons, preferably 1-4 carbons), acrylic acid and glycidyl acrylate or methacrylate.

U.S. Patent No. 3,299,010 to Samour describes a variety of adhesive compositions, some of which contain
10 C-12 to C-24 residues. The patent teaches that the higher alkyl residues must be branched in order to avoid crystallinity. Some of the compositions contain acrylamido or other polar groups, and claims of adhesion to moist skin are made.

U.S. Patent No. 3,535,195 to Davis et al.
15 describes a pressure-sensitive, amine-containing adhesive which is stated to exhibit good tack yet be easily removable from a substrate.

U.S. Patent No. 3,635,754 to Beede describes a
20 temporary pressure-sensitive polyolefin-based adhesive product which is activated by heating at least 15°C above its melting point, and which, after cooling, remains tacky for an extended but unpredictable period of time.

U.S. Patent No. 3,690,937 to Guse et al.
25 relates to pressure-sensitive adhesives formulated from di-alkyl fumarates.

U.S. Patent No. 3,838,079 to Kosaka et al.
describes copolymer resins prepared from alkyl acrylates (1-20C) and maleic anhydride.

U.S. Patent No. 3,922,464 to Silver et al.
30 describes an adhesive tape which apparently may be removed "cleanly" from a substrate. The improvement is stated to reside in the use of a novel combination of monomers, including 88-99 parts by weight of at least one
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terminally unsaturated vinyl monomer, .2 to 5 parts by weight of at least one emulsifier monomer, and 0-10 parts by weight of at least one zwitterionic monomer. The terminally unsaturated vinyl monomer is a nontertiary alkyl acrylate.

U.S. Patent No. 3,935,338 to Robertson describes a method for making pressure-sensitive adhesive compositions which comprises forming a hot-melt of a block copolymer containing monoalkynyl arene polymer blocks and an elastomeric conjugated diene block. Oil is included in the composition to reduce peel adhesion and shear adhesion failure temperature.

U.S. Patent No. 3,956,223 to Chiang et al. describes a hot-melt adhesive useful for forming adhesive devices such as tapes, films and the like, wherein the adhesiveness of the composition increases with warming.

U.S. Patent No. 3,975,323 to Georgoudis et al. describes a copolyester composition containing an aromatic dicarboxylic acid, a dimer acid, and a C₂ to C₁₀ glycol, and a polyester polyol. The resultant copolyester is stated to be useful as a hot-melt adhesive. Adhesion of the composition apparently increases with warming.

U.S. Patent No. 4,140,115 to Schonfeld is directed to an improved pressure-sensitive adhesive composition which is stated to be easily removable from the skin with a minimum of skin damage. The improved adhesive composition contains 4-20% by weight of an unreacted polyol, a water-absorbing agent.

U.S. Patent No. 4,151,319 to Sackoff et al. is also directed to adhesive additives which are stated to facilitate removal. The additive comprises a polysiloxane as set out, for example, in claim 1.

U.S. Patent No. 4,152,189 to Guerrin et al. describes polyacrylic hot-melt adhesives wherein warming of the composition apparently increases the degree of adhesion.

5 U.S. Patent No. 4,335,026 to Balinth describes a pressure-sensitive adhesive composition having decreased resistance to peel removal. The adhesive contains an elastomeric portion which is stated to achieve the desired peel adhesion. This elastomeric
10 fraction of the composition consists of a rubber, preferably a natural rubber, and a selected olefin terpolymer.

U.S. Patent No. 4,356,222 to Harakawa describes a fusion-bondable sheet comprising a crosslinked
15 polyolefin layer sandwiched between a fusion-bondable layer which is polyolefin-based and contains a tackifier, and a flame-retardant sheet.

U.S. Patent No. 4,487,872 to Takemoto et al. describes a composition which is stated to be readily
20 removable and repositionable. The adhesive contains a carboxyl-modified vinyl chloride-vinyl acetate copolymer, a polymeric polyester plasticizer, and a halo-organophosphorus plasticizer. It is stated that the desired adhesive bonding strength at the normal use
25 temperature may be controlled by adjusting the relative amounts of halo-organophosphorus plasticizer and polyester in combination with the vinyl monomer-containing copolymer.

U.S. Patent No. 4,728,572 to Davis describes a
30 hot-melt adhesive composition containing styrene-isoprene-styrene block copolymers, a low softening point highly aliphatic resin and a metallic salt of a fatty acid. The combination of materials is stated to
35 facilitate adherence to a variety of substrates, yet

provides a product which can apparently be readily and cleanly removed from substrates when desired. It appears to be the low softening point resin which provides the adhesive composition with the desired "clean removal" property. Also, note that the claims of the patent are specifically directed to paper labels.

U.S. Patent Nos. 4,762,888 and 4,879,178 to Sun et al. describe hot-melt adhesives comprising acrylic-based copolymers. One of the acrylic copolymers of the composition is stated to have a low glass transition temperature T_g , while the other has a high T_g .

U.S. Patent No. 4,783,354 to Fagan describes an adhesive sheet material which can apparently be readily removed from a surface. The adhesive composition contains a tacky pressure-sensitive adhesive, a wax, water and an emulsifier. The wax is apparently the component which provides the composition with its capability of being readily removed.

U.K. Patent No. 870,022, inventors Dahlquist and Zenk, teaches the use of a copolymer of octadecyl acrylate, acrylonitrile, ethyl acrylate, and acrylic acid as a low-adhesion backsize on a pressure-sensitive adhesive tape.

PCT Publication No. WO84/03837 teaches the use of copolymers which contain a polyalkylene oxide monomer in addition to acrylate. The polyoxyalkylene moiety is stated to impart hydrophilic behavior to the adhesive composition, thus facilitating adhesion to moist skin.

European Patent Application Publication No. 062682 describes the use of the monomer dodecyl methacrylate in a copolymer employed as an adhesive carrier for nitroglycerine. Small amounts of other comonomers (acrylic acid and short chain acrylates) are

added to the reaction mixture to improve the properties of the copolymer.

Japanese Patent Application No. 1240589 describes an adhesive tape which can apparently be peeled off the skin without causing pain or skin damage. The adhesive is hardened by UV rays and is formed from an acrylic adhesive composition containing a cyanurate compound or an isocyanurate compound.

Japanese Patent Application Nos. 56039014 and 84003966 describe a thermoplastic adhesive composition which may apparently be painlessly peeled off the skin. The composition contains styrene, methylstyrene or some other vinyl polymer having a glass transition temperature T_g higher than 70°C. The adhesive composition also contains a butadiene, isoprene or other conjugated diene compound.

Japanese Patent Application No. 59093771 describes an adhesive composition which is stated to lose tack upon warming. The composition contains a rubber component and a resol type phenol resin.

The following references specifically relate to side-chain crystallizable polymers: J. Polymer Sci.: Macromolecular Review 8:117 (1974) and J. Polymer Sci.: Polymer Chemistry Edition 19:1871-1873 (1981).

A PCT publication, WO91/14462, published October 3, 1991 refers to medical devices comprised of a substrate with a particular moisture vapor transmission rate with an adhesive thereon which is tacky at skin temperature but less tacky or not tacky at room temperature. A similar medical adhesive device is disclosed in WO91/14461. The disclosure of both of these PCT publications is incorporated herein by reference to the extent they disclose such devices including

particular backing layers, adhesives and methods of use and manufacture.

Flexible polymeric film materials are also known such as described in European Patent Applications Nos. 0107915 and 0147119 and PCT/GB91/00496. Those references describe materials with particular moisture vapor transmission rates which might be used as backing materials in connection with the present invention. Film materials which have moisture vapor transmission rates generally compatible with human skin are most preferred.

Disclosure of the Invention

The present invention provides unique pressure-sensitive adhesive compositions which can be made to exhibit an excellent four-fold balance of adhesion, cohesion, flexibility, and elasticity within a normal use temperature zone. Furthermore, the adhesives of the invention can be made to undergo a sharp imbalance in those properties at temperatures just below and/or above the normal use range. The novel adhesive compositions, by virtue of the exhibited imbalance, are selectively able to lose their adhesive property toward a substrate without losing their cohesive strength. Retaining cohesivity but losing adhesivity at temperatures outside the NUTZ enables an article bonded to a substrate with the adhesive composition to be removed therefrom without leaving any residual adhesive on the separated substrate.

The above-described properties suggest uses for these unique compositions of matter which derive from the fact that these pressure-sensitive adhesives require no significant force to remove them from a substrate but exhibit normal bond strength characteristics when used within the NUTZ. Such properties and characteristics are particularly attractive in medical products which are

affixed to the skin for a period of time and then must be removed, preferably without loss or damage to the skin and hair.

In one aspect of the invention, then, an
5 adhesive composition is provided for affixing an article to a substrate at a temperature within the normal use temperature zone (NUTZ) of the adhesive, the NUTZ being bound by a minimum and a maximum temperature, with a normal use temperature therebetween, wherein the
10 composition comprises:

(a) approximately 50 wt.% to 99 wt.% of a polymeric, pressure-sensitive adhesive component; and

(b) admixed intimately therewith, approximately
1 wt.% to 50 wt.% of a crystalline polymer that is
15 partially miscible with the polymeric, pressure-sensitive adhesive component, and has a heat of fusion of at least about 20 Joules/g,

such that the adhesive composition is tacky at temperatures within the NUTZ. Depending on the
20 embodiment, the composition will exhibit a lower tack value at temperatures below the NUTZ, a lower tack value at temperatures above the NUTZ, or both.

In another aspect of the invention, an adhesive assembly is provided which may be affixed to a substrate
25 at a temperature within an NUTZ as defined above, wherein the assembly itself is a body member having a surface coated with a temperature zone specific pressure-sensitive adhesive (TZS-PSA) comprising approximately 50 wt.% to 99 wt.% of a polymeric pressure-sensitive
30 adhesive component and, admixed intimately therewith, approximately 1 wt.% to 50 wt.% of a crystalline polymer as above and as will be discussed in detail herein.

In still another aspect, the invention is
35 directed to such adhesive assemblies which are

particularly suited for medical applications, i.e., which are useful for adherence to the skin. Adhesive assemblies for adherence to the skin preferably have a skin compatible moisture vapor transmission rate ("MVTR") of greater than about 100 g/m²/day (measured at approximately 37°C and a relative humidity difference of 100% to 10%).

In yet another aspect of the invention, a process is provided for affixing an article to the surface of a substrate at a temperature within a NUTZ wherein the process comprises interposing between the selected article and substrate surface a temperature zone specific, pressure-sensitive adhesive composition comprising approximately 50 wt.% to 99 wt.% of a polymeric pressure-sensitive adhesive component and, admixed intimately therewith, approximately 1 wt.% to 50 wt.% of a crystalline polymer in accordance with the invention.

In other aspects of the invention, processes are provided for rendering a polymeric adhesive composition tacky only within or above a particular NUTZ and for rendering a polymeric adhesive composition nontacky below a particular NUTZ, these processes comprising incorporating into polymeric adhesive compositions approximately 1 wt.% to 50 wt.% of a crystalline polymer in accordance with the invention.

Brief Description of the Figures

Figures 1 and 2 illustrate the temperature-variable behavior of adhesive compositions of the invention, and are described in detail in Example 40.

Modes for Carrying Out the Invention

Definitions and Terminology:

Before the adhesive compositions, assemblies and processes of the invention are described in detail, it is to be understood that this invention is not limited to particular adhesive components, i.e., specific pressure-sensitive adhesive polymer components or particular crystalline polymers, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present invention will be defined only by the appended claims.

It must be noted that, as used in this specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a side-chain crystallizable polymer" includes statistical mixtures of such polymers.

The term "tack" as used herein is intended to designate the tacky or sticky nature of certain adhesive compositions. Tack can generally be determined by what is referred to as the thumb test in which the thumb makes rapid and reversible contact with the surface being considered to determine the tacky or sticky nature of the surface. The Tack Rolling Ball Test (TRBT) designated as D3121 by the American Society for Testing and Materials and PSTC-6 (revision 8/85, incorporated herein by reference) by the Pressure-Sensitive Tape Council is also ideally suited for accurately and reproducibly measuring tack over wide temperature ranges. This test is described in detail in the Experimental section of this application, below.

The terms "tack" and "tacky" are qualitative. The tack of an adhesive film coating is affected by its thickness, especially when the coating is less than about .005 in thickness. Generally, tack increases directly
5 with thickness. The terms relating to the normalized value properties of an adhesive coating obtained by the TRBT tack determination method can be described as "tacky", "slightly tacky" and "substantially nontacky". These terms as used herein are intended to relate to
10 approximate values, respectively: (1) a tack value of greater than about 10^{-2} cm⁻²; (2) a tack value in the range of about 10^{-2} cm⁻² to 10^{-3} cm⁻²; and (3) a tack value of or below about 10^{-3} cm⁻² (with all tack values measured according to the aforementioned TRBT method).

15 The term "bond strength" between an adhesive-coated article and the substrate to which it is affixed is defined as the force required to separate those components. The term "substantially nonbonding" as used herein is intended to mean that very little if any force
20 is required to separate the aforementioned components.

The term "peel" as used hereinabove is intended to define the bond strength between an adhesive coated article and the substrate to which it is joined when those components are separated at a rate of 12 inches/min
25 unless otherwise noted and where the angle between separated components approximates 180°. The peel strength of an adhesive film coating is also affected by its thickness, especially when the coating is less than .005-inches thick. (In order to make meaningful
30 evaluations and comparisons in the regard, we have cast all coatings to a final dried thickness of between 1.6 and 1.8 mils.)

The term "pressure-sensitive" as used herein defines a distinct category of adhesives which, in
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solvent-free form, are aggressively and permanently tacky at use temperature and firmly adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure. Such adhesives are characterized by the "four-fold balance" of adhesion, cohesion, flexibility, and elasticity identified above, and are thus to be distinguished from various other products which possess some but not all of these properties. Products made with the TZS-PSAs of the invention exhibit PSA properties only within their specific temperature zone.

The terms "adhesion" and "cohesion" are used herein as follows. Adhesion is needed to affix the article on the substrate, with "adhesive bond strength" defined as the bond strength between the adhesive and the substrate. Cohesion is the counter force needed to prevent the adhesive layer from separating or pulling apart when one removes the article from the substrate to which it is bonded. Both adhesive and cohesive forces are required to maintain the union between the bonded substrate and substrate. Generally, it is desired that the cohesive strength is greater than the adhesive strength so that when the article is removed none of the adhesive remains on the substrate.

By the terms "melting point" or "first order transition temperature", as used herein, is meant the temperature at which an equilibrium process causes certain portions of the polymer, initially aligned in an ordered array, to become disordered. It is preferred that melting occur rapidly, i.e., over a relatively narrow temperature range, less than about 10 centigrade degrees, preferably less than about 5 centigrade degrees.

By "Normal Use Temperature Zone," or NUTZ, as explained above, is meant a temperature range whose

position and breadth are determined by factors such as the amount and nature of the crystalline polymer as well as the amount and nature of the pressure-sensitive adhesive component incorporated into the TZS-PSA, and encompasses the temperature range within which the TZS-PSA (1) maintain at least some tackiness and (2) bonds strongly to a substrate and retains both adhesive and cohesive strength. The adhesive compositions of the invention are tacky within at least part of the NUTZ defined by the particular crystalline polymer used. The normal use temperature zone varies and can be varied by changing the components and formulating the components in a desired manner. The resulting formulations have normal use temperature zones which are ranges within which the adhesive compositions of the invention: (1) have sufficient tackiness to allow the compositions to be applied, i.e., so that the compositions will initially stick and be tacky; and (2) have sufficient bonding strength to allow the compositions to form a fixed bond between two objects. The temperature range of a composition which allows for sufficient tackiness for application purposes and the temperature range for a composition which allows sufficient bonding strength can be, but need not be, the same. The normal use temperature zone encompasses both ranges for a given composition. Accordingly, a given composition may maintain its bonding strength over a broader range (especially at lower temperatures) than it initially maintains its tackiness for application and the normal use temperature zone encompasses both ranges, i.e., range for (1) tackiness and (2) range for bonding. Adhesive compositions of the invention do not generally have normal use temperature zones which extend above 120°C or below -10°C and more generally have narrow use

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temperature zones well within that range with the range and the position of the range being adjusted by adjusting the amounts and type of components within the formulation.

5 "Intimate admixture", as used herein to describe the physical relationship between the polymeric pressure-sensitive adhesive component and the crystalline polymer, is intended to mean thorough and pervasive physical combining of the two types of polymeric
10 components in the composition. "Intimate admixing" of the two polymeric components thus creates a three-dimensional physical network of admixed polymers.

The term "partially miscible" as used herein to describe the state of the two components herein when
15 admixed together to give the adhesive compositions of the invention is used in its conventional sense, to mean that at least part of the admixture has one phase in which both components are present. Other phases may be present. Partial miscibility of the two components
20 herein, at temperatures above the melting point or first order transition temperature of the crystalline polymer, is evidenced by cosolubility in common solvents or clarity of heated films made with the adhesive mixture (with extremely clear films indicating almost complete
25 miscibility). Partial miscibility of the two components, at temperatures below the melting point or first order transition temperature of the crystalline polymer, is evidenced by depression of that transition temperature upon admixture (thus implying at least partial co-crystallization).
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By the term "porous surface" is meant one which has numerous and sufficient pores and interstices that permit a significant penetration of portions of the viscoelastic adhesive composition with which it is in
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intimate contact. Examples of porous surfaces include paper, wood, Tyvec sheeting and skin.

By the term "nonporous surface" is meant one which has an insignificant number of pores and interstices to permit a significant penetration of portions of the viscoelastic adhesive composition with which it is in intimate contact. Examples of nonporous surfaces include glass, plastic, metal and enameled coatings.

The term "polymer" as used herein is intended to include both oligomeric and polymeric material, i.e. compounds which include two or more monomeric units.

The term "skin" as used herein is intended to encompass live human or animal skin or mucosal tissue.

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The TZS-PSAs of the Invention:

The present invention is thus premised on the discovery that the intimate admixture of a crystalline polymer having certain physical and chemical characteristics with a polymeric pressure-sensitive adhesive component gives rise to an adhesive composition that has temperature-controlled variability in adhesivity. That is, the incorporation into an adhesive composition of a partially miscible, phase-separated crystalline polymer with a particular melting point or first order transition temperature creates a specific temperature range, or NUTZ, within which the composition is tacky, with the melting point or transition temperature of the crystalline polymer being within the range. For nonporous substrates, an article bonded to a substrate with the novel adhesive composition can be removed by cooling to below the NUTZ. If lower molecular weight crystalline polymers are used, i.e., crystalline polymers having a molecular weight of below about 25,000

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Daltons, one can remove the article by either cooling to below the NUTZ or, alternatively, heating to above the NUTZ. For porous substrates, an article bonded to a substrate with the novel adhesive composition cannot be removed by cooling to below the NUTZ unless the composition is cured (crosslinked) to a slight but sufficient degree, so as to prevent significant penetration into the substrate of the viscoelastic adhesive composition with which it is in intimate contact. Hence, when cured compositions are used employing lower molecular weight crystalline polymers, i.e., crystalline polymers having a molecular weight of below about 25,000 Daltons, the article can be removed by either cooling to below the NUTZ or, alternatively, heating to above the NUTZ.

The polymeric pressure-sensitive adhesive component of the present compositions may be any PSA which, in solvent-free form, is aggressively and permanently tacky and firmly adheres to a variety of dissimilar surfaces upon mere contact, as explained above. This polymeric pressure-sensitive adhesive component, sometimes referred to herein as the "majority" component of the adhesive compositions of the invention, must be such that it does not react or otherwise interact in a deleterious manner with the crystalline polymer. Examples of pressure-sensitive adhesives useful as the majority component of the present compositions include, but are not limited to: natural rubber adhesives; styrene/butadiene latex-based adhesives; thermoplastic rubbers of the A-B-A block copolymer type (where A represents a thermoplastic polystyrene end block and B represents a rubber midblock of polyisoprene, polybutadiene or poly(ethylene/butylene)); butyl rubber; polyisobutylene; acrylic adhesives such as polyacrylates

and vinyl acetate/acrylic ester copolymers; and polymers and copolymers of vinyl ethers such as polyvinylmethyl ether, polyvinylethyl ether, and polyvinylisobutyl ether. This PSA component may be a polymer or a simple mixture
5 of polymers or it may be a polymeric composition containing plasticizers, tackifiers, fillers, stabilizers or the like. It is preferred that this majority component of the present adhesive compositions represent on the order of 50 wt.% to 99 wt.% of the adhesive
10 admixture, preferably 65 wt.% to 95 wt.%, more preferably 70 wt.% to 90 wt.%, and most preferably 70 wt.% to 80 wt.%.

This polymeric pressure-sensitive component need not exhibit all the characteristics of a PSA at
15 normal room temperature provided that those characteristics develop at or just below a specific higher temperature for which their use is intended. The component may exhibit nonadhesive rubbery, glassy or crystalline properties at room temperature, yet upon
20 warming become tacky and adhesive. The transition from a non-PSA to a PSA-like material may be triggered by an inherent characteristic of the material such as by its melting point or by the presence of one of the crystalline polymers of the invention.

25 The major factors which are thought to be important in these "precursor PSAs" which may be used as the majority component herein are the same as in conventional PSAs, namely, a high degree of compatibility in the casting or forming process, and the ability to
30 allow phase separation with regard to and co-crystallize in part with the crystalline polymer. Additionally, these precursor PSAs must show a resistance to flow within an elevated use temperature zone (EUTZ). Resistance to flow may be attained by covalent or ionic
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crosslinking, incorporation of block co-polymers, strong hydrogen bonding, polymer chain entanglement, use of high glass transition co-monomers, and other known methods.

Where the majority component is such that it becomes a PSA-like material in combination with the crystalline polymer component, the latter component, while below its melting point or first order transition temperature, will have no or little effect on the stiff and nontacky precursor PSA. However, the crystalline polymer component when molten will act as an effective plasticizer for the precursor PSA rendering it tacky without lowering its resistance to flow.

Where the majority component is such that it becomes a PSA-like material upon triggering an inherent characteristic of the material, such as by heating to above its melting point, it is generally desired for the precursor PSA to accomplish this transition several degrees below the melting point of the crystalline polymer. The combination of the molten precursor PSA and the crystalline polymer in the EUTZ must exhibit sufficient cohesive strength so that it may be a strong adhesive at those temperatures. Above the EUTZ, the crystalline polymer component melts and reduces the adhesive bond strength without greatly reducing the cohesive bond strength. Thus, the adhesive is removed easily and cleanly if desired.

For example, materials such as Elvax[®] 240, other polyolefin-based adhesives, polystyrene and the like, are not normally tacky at room temperature and are not generally regarded as PSAs. Indeed, they are by their own nature, crystalline or glassy polymers. However, when their crystalline melting point or glass transition temperature is exceeded, they may become tacky, PSA-like materials. Specifically, if the

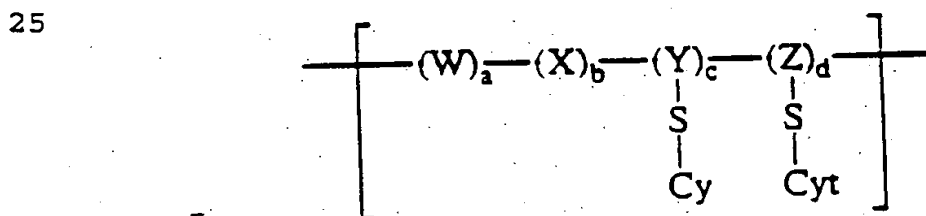
temperature of partially crosslinked Elvax[®] 240 is raised to above about 60°C, such that its melting point is exceeded, there will be sufficient polymer melting to permit wetting of the surface, much like a conventional PSA at room temperature. Used at this elevated temperature, articles can be securely bonded to a substrate because there is adequate cohesive strength within the molten component. Upon removal of the article from the substrate, however, it is likely that much of the adhesive would remain on the surface of the elements. If a crystalline polymer (whose melting point or first order transition temperature was about 70°C) as will be described in detail below had been admixed with the precursor PSA, then heating the molten adhesive composition still higher to above the NUTZ would result in a clean bond failure, leaving little or no adhesive on the bonded elements.

Alternatively, if a sample of polystyrene were heated which had been lightly crosslinked using, for example, divinyl benzene, it will become mobile above its glass transition temperature of 100°C and have the properties of a pressure-sensitive adhesive at those elevated temperatures. If then a crystalline polymer of the present invention having a melting point of 120°C is incorporated into the polystyrene, then this combination will behave as a TZS-PSA of the invention in that the adhesive strength of the PSA will be substantially reduced at temperatures above 120°C when compared to the adhesive peel strength value at, say, 110°C.

The crystalline polymer which is intimately admixed with the majority component is partially miscible therewith and, at temperatures below the melting point or first order transition temperature of the crystalline polymer, is phase-separated therefrom. The crystalline

polymer represents about 1 wt.% to 50 wt.%, preferably 5 wt.% to 35 wt.%, more preferably 10 wt.% to 30 wt.%, and most preferably 20 wt.% to 30 wt.% of the adhesive admixture. The desired amount of crystalline polymer in the adhesive composition will depend on several factors. With some systems, less crystalline polymer is required. For example, when acrylate polymers are used, as little as 0.5 wt.% to 1 wt.% polymer is necessary. Additives can also influence the amount of crystalline polymer required -- incorporation of a plasticizer or tackifier such as polybutene, for example, can reduce the quantity of crystalline polymer that is needed.

Typically, the crystalline polymer has a melting point or first order transition temperature which defines the NUTZ of the composition, with the melting point or first order transition temperature between the minimum and maximum temperatures of the NUTZ. The crystalline polymers may be either side-chain crystallizable ("SCC") polymers or main-chain crystallizable ("MCC") polymers, with the former group preferred. The side-chain crystallizable polymers that are most preferred in connection with the present invention contain recurring units having the structural formula



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wherein W and X are each respectively a first and a second monomer unit, which monomer unit may be any molecular moiety connectable to an adjoining molecular moiety (i.e., polymerizable), Y and Z are each

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independently a backbone monomer unit which may be any molecular moiety or atom, each S is independently a linking group or spacer unit and is optionally present, Cyt and Cy are each independently a crystallizable moiety
5 connected to the respective backbone directly or via the spacer unit, and a, b, c, and d are each, independently, integers ranging from 0-1,000 with the proviso that sufficient Cyt and Cy are present so as to provide a Mw which is equal to or greater than twice the sum of the
10 Mws of W, X, Y and Z, and further wherein the polymers have a heat of fusion (ΔH_f) of at least about 20 Joules/gram. It is understood that when the variables a, b, c and d are greater than 1, the monomer units W, X, Y and Z can be repeating units or mixtures of different
15 monomer units. For example, if a is 100, W could be a mixture of styrene, vinyl acetate, acrylic acid, methyl styrene and hexadecyl acrylate in ratios of 5:5:2:5:83. Thus, any of the monomer units W, X, Y and Z can be mixtures of polymerizable monomers.

20 The adhesive compositions of the invention are optionally crosslinked. Crosslinking may be effected using any of the known techniques, e.g., via crosslinking agents, heating, radiation, or the like. Crosslinked adhesive compositions are particularly preferred when
25 used for bonding articles to porous substrates, so that bonded articles may be removed therefrom upon cooling to a temperature below the NUTZ.

The backbone of the polymer (defined by W, X, Y and Z) may be any organic structure (aliphatic or
30 aromatic hydrocarbon, ester, ether, amide, etc.) or an inorganic structure (sulfide, phosphazine, silicone, etc.). The spacer linkages can be any suitable organic or inorganic unit, for example ester, amide hydrocarbon, phenyl, ether, or ionic salt (for example a carboxyl-
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alkyl ammonium or sulfonium or phosphonium ion pair or other known ionic salt pair). The side-chain (defined by Cyt and Cy and an optional present S) may be aliphatic or aromatic or a combination of aliphatic side-chains of at least 10 carbon atoms, fluorinated aliphatic side-chains of at least 6 carbons, and p-alkyl styrene side-chains wherein the alkyl is of 8 to 24 carbon atoms.

The length of each side-chain moiety is usually greater than 5 times the distance between side-chains in the case of acrylates, methacrylates, vinyl esters, acrylamides, methacrylamides, vinyl ethers and alpha olefins. In the extreme case of a fluoroacrylate alternate copolymer with butadiene, a side chain can be as little as 2 times the length of the distance between branches. In any case, the side-chain units should make up greater than 50% of the volume of the polymer, preferably greater than 65% of the volume. Co-monomers added to a side-chain polymer usually have an adverse effect on crystallinity. Small amounts of various co-monomers can be tolerated, usually up to 10 to 25 volume percent. In some cases it may be desirable to add a small amount of co-monomers, for example cure site monomers such as acrylic acid, glycidal methacrylate, maleic anhydride, amino functional monomer and the like.

Examples of side-chain crystallizable monomers within the aforementioned are the acrylate, fluoroacrylate, methacrylate and vinyl ester polymers described in J. Poly. Sci. 10:3347 (1972); J. Poly. Sci. 10:1657 (1972); J. Poly. Sci. 9:3367 (1971); J. Poly. Sci. 9:3349 (1971); J. Poly. Sci. 9:1835 (1971); J.A.C.S. 76:6280 (1954); J. Poly. Sci. 7:3053 (1969); Polymer J. 17:991 (1985), corresponding acrylamides, substituted acrylamide and maleimide polymers (J. Poly. Sci., Poly. Physics Ed. 18:2197 (1980)); poly (α -olefin) polymers such

as those described in J. Poly. Sci.: Macromol. Rev. 8:117-252 (1974), and Macromolecules 13:12 (1980), polyalkylvinylethers, polyalkylethylene oxides such as those described in Macromolecules 13:15 (1980),
5 alkyphosphazene polymers, polyamino acids such as those described in Poly. Sci. USSR 21:241 (1979), Macromolecules 18:2141 (1985), polyisocyanates such as those described in Macromolecules 12:94 (1979), polyurethanes made by reacting amine- or alcohol-
10 containing monomers with long-chain alkyl isocyanates, polyesters and polyethers, polysiloxanes and polysilanes such as those described in Macromolecules 19:611 (1986), p-alkylstyrene polymers such as those described in J.A.C.S. 75:3326 (1953) and J. Poly. Sci. 60:19 (1962),
15 and triglycerides such as tristearin or pentaerythritol tetrastearate.

Particularly preferred side-chain crystallizable polymers for use herein are linear aliphatic C₁₄-C₅₀ acrylates, linear aliphatic C₁₄-C₅₀
20 methacrylates, linear aliphatic C₁₄-C₅₀ acrylamides, and linear aliphatic C₁₄-C₅₀ methacrylamides. Most preferred within this group are linear aliphatic C₁₆-C₂₂ acrylates, linear aliphatic C₁₆-C₂₂ methacrylates, linear aliphatic C₁₆-C₂₂ acrylamides, and linear aliphatic C₁₆-C₂₂
25 methacrylamides.

As alluded to above, the melting point or first order transition temperature of the crystalline polymer selected defines a normal use temperature zone, or NUTZ, within which the composition is tacky. Thus, for
30 example, a C₁₄ acrylate which has a first order transition temperature of about 20°C will give rise to an NUTZ approximately centered around a few degrees below 20°C. The amount of the crystalline polymer incorporated into the adhesive composition has surprisingly little
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effect on the position or the breadth of the range. However, the amount does greatly influence the bond strength both within and above the NUTZ. For example, an acrylic based formulation containing 15, 25, 35 and 55% of the C16 SCC referenced (as demonstrated in the examples below and shown in Table 4) show peel strengths of 67.4, 61.7, 72.5, and <15 g/cm when measured within the NUTZ but exhibit peel strengths of only 58, 16.1, 20.1 and <15 g/cm when measured above the NUTZ. There is no significant difference in bond strength within the NUTZ when loadings are held between 15 and 35%. However, when the temperature is raised above the NUTZ, only a 14% reduction in bond strength is observed at a 15% loading, while at 25 and 35% loading, a greater than 72% reduction is observed. Thus, selection of the specific polymer and the particular quantity incorporated into the total composition defines the median temperature of the NUTZ as well as the magnitude of the effect. The optimum loading must therefore be determined on a case-by-case basis, and is selected so as to afford the highest peel strengths within the NUTZ and the greatest reduction of peel strengths above (and, for some applications, below) the NUTZ. The following table sets forth particular transition temperatures of selected side-chain crystallizable polymers:

Table 1

	<u>Polymer</u>	<u>Transition Temperature, °C</u>
	C ₁₄ Acrylate	20
5	C ₁₄ Methacrylate	10
	C ₁₆ Acrylate	36
	C ₁₆ Methacrylate	26
	C ₁₈ Acrylate	49
	C ₁₈ Methacrylate	39
	C ₂₀ Acrylate	60
	C ₂₀ Methacrylate	50
	C ₂₂ Acrylate	71
10	C ₂₂ Methacrylate	62
	C ₃₀ Acrylate	76
	C ₃₀ Methacrylate	68
	C ₄₀ Acrylate	96
	C ₄₀ Methacrylate	91
	C ₅₀ Acrylate	102
15	C ₅₀ Methacrylate	95

In order to provide an adhesive composition with an NUTZ in the range of say 20°C to 40°C, one would select a crystalline polymer which is partially miscible with the majority component of the composition, having a melting point or first order transition temperature of about 30°C, with the amount of polymer selected so as to give a range of 10°C above and below 30°C.

The crystalline polymers used herein may also be main-chain crystallizable polymers, i.e., polymers which are rendered crystallizable by their backbone structure (whereas side-chain crystallizable polymers contain crystallizable side-chain moieties as described above). Preferred main-chain crystallizable polymers include water insoluble polyalkylene oxides, lower alkyl polyesters, polyamides, nylons and polytetrahydrofuran, and particularly preferred main-chain crystallizable polymers for use herein are poly- α -olefin polymers containing recurring units having the structural formula



wherein R is hydrogen or C₁-C₁₂ linear or branched alkyl, more preferably C₁-C₈ linear or branched alkyl. R may
5 be, for example, hydrogen, methyl, propyl, butyl, pentyl, 4-methyl pentyl, hexyl and heptyl.

Crystalline polymers useful herein may be obtained commercially or they may be chemically synthesized. For methods of synthesizing side-chain
10 crystallizable polymers, reference may be made to E.F. Jordan et al., "Side Chain Crystallinity II", J. Polym. Sci., Part A-1, 9:3351 (1971). Particular methods of making crystalline polymers are also described in detail in the examples herein.

15 Hydrophilic monomers are beneficially incorporated in the polymer if it is desired to increase the MVTR properties of the adhesive. Commonly used hydrophilic comonomers include acrylic acid, acrylamide, hydroxy alkyl (meth)acrylates such as hydroxy ethyl
20 acrylate, hydroxy ethyl methacrylate and hydroxy butyl acrylate, alkoxy (meth)acrylates such as ethoxy ethyl acrylate, ethoxy ethoxy ethylacrylate, ethyltriglycol methacrylate, 3-methoxy butylacrylate and the like. A preferred class of high MVTR inducing monomers are
25 derivatives of polyethylene glycol with molecular weights ranging from 50 to 5,000. Commonly these units may be incorporated either into the backbone or as pendant groups.

- Moisture vapor transmission rates and/or
30 absorptive properties of the adhesive may also be modified by the incorporation of soluble or insoluble hydrophilic materials, for example, by addition of carboxymethyl cellulose, guar gum, carrageenan, cellulose-based or synthetic fibers and the like.
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All of the aforementioned TZS-PSA compositions of the invention are tacky within the particular NUTZ defined by the crystalline polymer, may be substantially nontacky below the NUTZ, and display an extremely rapid transition between the tacky and substantially nontacky states.

The particular molecular weight of the crystalline polymer used is an important factor in determining how the adhesive compositions of the invention will display temperature-variable tack and/or adhesive bond strength. That is, in general, lower molecular weight crystalline polymers will give rise to an adhesive composition which loses bond strength upon heating, i.e., when heated to a temperature above the NUTZ, the composition then becomes substantially nonbonding. When this feature is desired, it is preferable to use crystalline polymers having a molecular weight of less than about 25,000 Daltons, more preferably in the range of about 3,500 to 25,000 Daltons, and most preferably in the range of about 3,500 to 12,000 Daltons. Compositions prepared using these relatively low molecular weight crystalline polymers may also be removed from a substrate by cooling to below the minimum temperature of the NUTZ. With higher molecular weight polymers, i.e., crystalline polymers having a molecular weight greater than about 25,000 Daltons, more typically in the range of about 25,000 to 900,000 Daltons, and most typically in the range of about 100,000 to 900,000 Daltons, the compositions may be removed from a substrate upon cooling to below the NUTZ, but do not share the feature of the compositions containing the lower molecular weight crystalline polymers in that they may not be removed from a substrate by heating.

Porosity of the substrate is also a factor in determining how the adhesive compositions of the invention may be used. That is, the removability of the present adhesive compositions upon cooling requires that the substrate be substantially nonporous, i.e., so that the composition has not penetrated into the interior of a substrate, but rather has remained substantially on the surface, as a coating. With porous substrates, clearly, the adhesive compositions of the invention are still substantially nontacky below the NUTZ, i.e., prior to application to the substrate, but they may not be removed upon cooling unless they are lightly cross-linked before application. Examples of porous and nonporous substrates are set forth above in the definitions section.

The adhesive compositions useful herein may include, in addition to the PSA component and the crystalline polymer, conventional additives such as tackifiers (wood rosin, polyesters, etc.), antioxidants, fibrous or nonfibrous fillers, colorants, and the like. It is also possible to include additional adhesive components and/or additional crystalline materials providing that the desired NUTZ profile is not significantly affected.

The adhesive compositions of the invention may be prepared by admixing the polymeric pressure-sensitive adhesive component and the crystalline polymer in a compatible solvent and adding optional components such as plasticizers, tackifiers, fillers, or the like. The solids content is adjusted to the desired viscosity, and the mixture is blended until it is homogeneous. Bubbles are removed from the mixture after blending. Reference may be had to the experimental section herein for information concerning the particulars of equipment, manufacturing conditions, and the like.

Methods of Use:

The adhesive compositions of the invention are useful in bonding an article to the surface of a substrate by, typically, first coating either the article or the substrate or both and then maintaining contact between the article and the substrate until affixation is effected. Coating to provide tapes, labels or the like may be done in any number of ways, e.g., by spray deposition, painting, dipping, rolling, or the like. The adhesive composition may also be applied by transfer from a release sheet in a manner similar to that involved in transfer printing. The composition may be applied neat or in a suitable solvent.

Affixation, because of the temperature requirements of the present compositions, must be carried out at a temperature within the NUTZ, i.e., at a temperature at which the adhesive composition is tacky. Provided that the substrate is nonporous as defined above, or that the adhesive composition used is, at least, partially cured, the affixed article may be removed upon cooling to a temperature below the NUTZ, e.g., upon application of ice or a cold pack, or, if a lower molecular weight crystalline polymer is used, the article may be removed by heating as well.

These features lend themselves to products such as removable wallpaper, removable price and bar code labels, and the like, which would be well-adhered to walls or merchandisable products at normal room temperature but could be easily removed when heated or cooled outside the normal use temperature, e.g., $>45^{\circ}\text{C}$ or $<15^{\circ}\text{C}$. There is also a need for a tape product that could serve to cover or hold an item securely in place on a substrate at a particular temperature use zone for an

indefinite period of time as well as a need to remove that item, with little or a minimum of force, upon demand, without leaving any adhesive residue or without damaging the surface of the substrate.

5 Furthermore, products made from these adhesives would find use in dermally related medical product applications. As such, they could be found in hospitals, first aid cabinets and medical supply inventories from whence they would be applied to normal skin which, incidentally, exhibits a remarkably well-defined, narrow
10 temperature range of 32°C to 36°C. When removal is desired, the affixed products could effortlessly be released from both hair and skin by raising the temperature to above about 40°C. Thus, common articles normally found in medical supply inventories such as
15 bandages, tapes, IV straps, wound closures and the like could be made with the adhesives of the present invention so that they would enjoy their current service function but could be removed cleanly and without the pain, hair removal, discomfort and epithelial cell damage commonly
20 associated with adhesive-removal trauma. Other medical applications include binding immobilization devices, transdermal drug delivery devices, surgical dressings, EKG electrodes, etc., to the skin.

25 Another specific area of use is in adhesive tapes and bandages. Here it is important to keep a dressing, or hold an IV line securely in place during the use phase of the adhesive.

In adhesive tapes and bandages, the backing
30 onto which the adhesive composition is coated may comprise any number of backings which are well known in the medical or surgical fields, including woven or nonwoven fabric, paper, synthetic film, and the like. While not required, flexibility or stretchability is
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preferred to ensure conformability to the skin such that full contact is made.

Particularly preferred medical adhesive assemblies are in the form of tapes and bandages which keep water and bacteria out while allowing the exchange of water vapor. This can be accomplished in a number of ways but is generally obtained by starting with a backing layer having a moisture vapor transmission rate (MVTR) of above 500 g/m²/day at 37°C and at a 100% to 10% relative humidity difference. The MVTR can be reduced by the adhesive. However, the backing substrate and adhesive can be chosen so that the MVTR of the final assembly is more than 100 g/m²/day, and the MVTR of the adhesive itself is at least about 300 g/m²/day, more preferably 500 g/m²/day. (Knowing the MVTR of a substrate and a product, the MVTR of the adhesive can be calculated using the formula

$$d^{-1} = b^{-1} + c^{-1}$$

20

where d is the MVTR of the entire assembly, b is the MVTR of the backing, and c is the MVTR of the adhesive layer.) If the bandage is, for example, in a large rectangular shape, the adhesive can be applied along the edge in a strip-like fashion so that the adhesive will not affect the MVTR of the majority of the bandage where no adhesive is present.

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Useful backing materials may be woven cloth treated to resist moisture; Gortex™-type materials or polyether polyester thermoplastic copolymers having characteristics as described above. An example of a useful backing is known commercially as Hytrel™ which is manufactured by DuPont. Also useful are polyether polyamides such as Pebax™ manufactured by ATO Chemical

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Co. and polyether polyurethanes such as Estane™ manufactured by Goodrich Chemicals Inc. The particular form of the backing used can be chosen by checking manufacturer specifications regarding MVTR and/or by testing the material using known testing methods. The thickness of the backing layer can, of course, have a substantial effect on the MVTR of the layer. A sheet of Estane™ having a thickness of about 25 μm will have a MVTR of about 1800 GSM and can be used as a backing layer in connection with the present invention. Other useful backing materials included 1,2-polybutadiene films sold by Japan Synthetic Rubber Company as RB810, RB820, and RB830 having a thickness of about 150 μm , and microporous polyolefins such as Celgard® (available from Hoechst-Celanese).

The invention, by virtue of the temperature behavioral variability of adhesion addressed at length above, also encompasses methods for rendering a polymeric adhesive composition tacky within a particular range of temperatures or for rendering a polymeric adhesive composition nontacky below a predetermined use temperature. These methods of use involve incorporation of the crystalline polymers described above into the polymeric adhesive composition, wherein the crystalline polymer is selected so that the NUTZ is as desired.

While not wishing to be bound by theory, it is postulated by the inventors herein that the difference in solubility parameters (or relative polarity) between (1) the crystalline polymer component and (2) the PSA component, both as defined herein, is closely related to the temperature-variable behavior of the composition on which the present invention is predicated. That is, it appears that when the difference in solubility parameters between the crystalline polymer and the adhesive

composition as a whole is within a certain range, the desired temperature-variable behavior of the adhesive composition is achieved. For example, it has been found that the following relationship should be met in order to
5 optimize the behavior of the present adhesive composition with certain metallic substrates:

$$\delta_1 - .5 \leq \delta_2 \leq \delta_1 + 1.5.$$

10 In the equation, δ_1 represents the solubility parameter of the base adhesive, and δ_2 represents the solubility parameter of the crystalline polymer (for purposes of the aforementioned relationship, solubility parameter units are in $J^{1/2}/cm^{3/2}$). A similar relationship is believed
15 to be operative with other substrates.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to formulate the adhesive compositions of the invention and make
20 articles which use such adhesive formulations and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should
25 be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C and pressure is at or near atmospheric.

Experimental

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A. Adhesive Drawdown Coating Procedure

Equipment: Wet film applicator rod (e.g., a 70" wire wound rod); 18" x 12" glass plate; laboratory roller mill; vortex mixer.

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Supplies: Adhesive materials (e.g., commercial acrylate adhesive, adhesive compounding additives and enhancers; if presolvated, each material should have a known solids content); organic solvents (generally heptane and toluene); backing substrate/film (generally 1.0 mil Mylar® film); glass mixing containers with foil or Teflon® screw caps (generally 2 to 8 ounce capacity); disposable plastic pipettes.

Coating Solution Preparation: 1. Glass containers were cleaned and tared, and labeled with an identification number. Containers were checked to ensure that they were free of dust and dirt and completely dry before continuing. 2. The desired amounts of adhesives and crystalline polymers were weighed out in a glass container, and the masses were recorded. 3. Optional additives were added at this point, and the mass of each added material recorded. 4. Organic solvent was added, as necessary, to cut solution viscosity. 5. The glass container was sealed, and the vortex mixer was used to blend the materials into a homogeneous solution. 6. The glass container was placed on the laboratory roller mill and the solution was rolled until all gas bubbles were removed.

Adhesive Coating Preparation: 1. The backing substrate was placed on a clean glass plate, and smoothed to remove air bubbles between the film and the plate. 2. The wet film applicator rod was placed on the portion of film furthest away from the operator. 3. A bead of coating solution was poured along the length of the wet film applicator rod, and the rod was pulled through the solution over the backing film without allowing the rod to spin or rotate. The rod should contact the film under its own weight. While coating, no additional pressure

was applied, downward or upward. 4. The coating was allowed to air dry.

B. Specific Coating Techniques

5 All adhesive materials were coated using the basic procedures as outlined under the "Adhesive Drawdown Coating Procedures" above. Below is a more concise version of the coating technique used.

10 The base adhesive (Morstik® 103) is commercially available in presolvated form at a known solids content (45%). A weighed amount of adhesive was poured into a glass jar. Added to the adhesive was the desired amount of crystalline polymer which was presolvated in heptane at 50% solids. The appropriate
15 amount (generally 15 phr) of lanolin (100% solids) was added. Then, toluene was poured in to lower the solids content of the coating solution to approximately 45%. This solution was vortexed until homogeneous and allowed to roll to remove the entrapped gas bubbles. Once the
20 solution was free of bubbles, it was ready for coating.

Depending on the application, the backing substrate can be either be 1.0 mil Mylar® or 1.75 mil Hytrel® 4056. Any coating used on skin had a Hytrel backing. All peel tests off of stainless steel used a
25 Mylar® backing, unless otherwise noted. The film was placed on a glass plate and secured down.

A drawdown coating was made using #70 Wire Wound Rod (Gardco® Wet Film Applicator Rod). This coating was air dried for 10 minutes and placed in a 90°C
30 oven for 15 minutes (minimum). Either siliconized Mylar™ film or a siliconized Polyethylene-impregnated paper (H.P. Smith Poly Slik L (275)) was laminated onto the coating to protect it from the environment (i.e., dust
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and dirt). The Poly Slik was only used when a Hytrel backing was required.

These laminations were cut to the appropriate size and measured for coating thickness, typically 1.6 to 1.8 mils thick. The samples had outside dimensions of 5.0 inches long x 1.0 inch wide. (See Section D below for specifications on Peel Test Specimen.)

C. Adhesive Drawdown Coating - Detail

Most Commercial Acrylate Adhesives (CAAs) used in these applications were dissolved in a multi-solvent solution. The solvent systems generally contained a polar and a nonpolar component. For example, the Gelva® 737 adhesive had a solvent system consisting of ethyl acetate (53%), toluene (11%) and ethanol (36%).

In order to incorporate the crystalline polymer into the CAAs, polar components had to be removed from the solution. The nonpolar nature of the crystalline polymer created an incompatibility between it and the base adhesive polymer. Hence, the polar solvent components were removed (by rotary vacuum evaporation) from the adhesive solution and replaced with a nonpolar solvent. The preferred method of handling this process was as follows:

(1) A known amount of adhesive solution was poured into a round bottom flask. The amount of polar solvent contained in the solution was calculated and an equal amount of nonpolar solvent was added, i.e., toluene, and thoroughly mixed.

(2) The flask was placed on a Buchi Rotovapor-R and securely fastened thereon. Solvent was driven off by applying heat and vacuum to solution. Evaporation of solvent was continued until the solution returns original mass (prior to the addition of the nonpolar solvent).

The temperature of the adhesive solution was not allowed to increase above 45°C, preferably 40°C. An aspirator operating between 60 to 76 cm Hg was used to supply the vacuum to the system.

- 5 (3) The solids content of the solution was rechecked and findings recorded.

D. Peel Strength and Tack Measurements

Peel strength was measured by two different methods. One employed an Instron Materials Testing Instrument (IMTI), the other, an Instrumentors Slip/Peel Tester (ISPT). All peel strength tests were completed using the IMTI where skin was the adherent surface. All other peel strength tests were completed using the ISPT.

15 IMTI Peel strength:

Peel strength was measured as follows. The adhesive solution was coated as outlined in the Adhesives Drawdown Coating Procedure. In addition, all coatings were dried in an oven for 0.25 hours at 90°C. Dried coatings were cooled for 0.50 to 0.75 hours at room temperature. The adhesive coating was cut into 0.5" x 5.5" strips which were applied to the underside of the forearms of 6 individuals. Two strips were placed lengthwise parallel to radius and ulna (the arm bones). After the strips were applied, light pressure was applied with a hand over the entire surface of the strips. The strips were allowed to remain on the arm for 4 hours. To determine the peel strength, each strip was connected to the load cell of the IMTI via a wire and clip and peeled back over itself at a 180° angle. Just prior to peeling, one of the strips was heated above the NUTZ with a commercial hair dryer and then immediately peeled off the arm. The average peel strength was measured at 10"/min.

35 ISPT Peel Strength:

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Peel strength was measured as follows. An Instrumentors, Inc. SP-102B Slip/Peel Tester was used according to the test procedure designated as PSTC-1 (revision 8/85) by the Pressure-Sensitive Tape Council (PSTC) and was calibrated and operated according to the instruction manual accompanying the instrument. In addition, all coatings were dried in an oven for 0.25 hours at 90°C. Dried coatings were cooled for 0.50 to 0.75 hours at room temperature. Individual specimens were cut lengthwise (generally 0.5 in. x 5.0 in. strips) in the direction of extrusion (of the backing substrate). Each specimen was gauged for coating thickness to the nearest 0.1 mil. At least three (3) points on each specimen were measured and the average of these points was considered the thickness value. Each testing specimen did not have greater than 0.25 mil variation from the thinnest point to the thickest point and the variation between thickness values of all the testing specimens did not exceed 0.25 mils. The average of the specimen thickness values (to the nearest .001 inch) was the reported coating thickness. The peel test was conducted as soon as possible after measuring coating thicknesses. The testing surface was stainless steel according to the specifications outlined in Appendage B of the Test Methods for Pressure-Sensitive Tapes by the PSTC and a 0.012 inch thick polyurethane film of Tuftane 410 (Lord Corporation, Erie, PA) which was secured to the temperature-controlled platen by means of double-sided carpet tape. Each specimen remained on the testing surface for 5 minutes before testing at the prescribed temperature of testing. Ten specimens were tested at each specific temperature. Each specimen was rolled with a 4.5 pound rubber roller immediately after contact with testing surface. The roller traveled over the surface of

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the specimen at a rate of 12 inches/min in both directions. The average peel force and terminal surface temperature was recorded.

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Example 1

This example demonstrates the preparation of a low molecular weight SCC polymer. Four hundred twenty-five (425) grams of octadecylacrylate, 65 grams of butylacrylate, 10.5 grams of acrylic acid, 5.0 grams of azobisisobutyronitrile (AIBN), and 25 grams of dodecyl mercaptan were combined with 1000 ml of toluene, purged with nitrogen and allowed to react for 12 hours at 80°C. The resulting solution was precipitated into methanol and dried. The molecular weight of the polymer, as determined by GPC analysis, was 7900 Daltons.

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Examples 2-4

Other synthesized low molecular weight SCC polymers were synthesized following the general procedure of Example 1:

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Table 2

25	<u>Monomer Content (%)</u>			<u>Molecular Weight</u> <u>(K = 1000)</u>
	<u>Docosyl-</u> <u>acrylate</u>	<u>Octadecyl-</u> <u>acrylate</u>	<u>Butyl-</u> <u>acrylate</u>	
Example 2		94	6	6.1 K (Low)
30 Example 3		97	3	6.5 K (Low)
Example 4	100			7.5 K (Low)

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Example 5

This example demonstrates the preparation of a high molecular weight SCC polymer. Five hundred eighty-eight (588) grams of octadecylacrylate, 12 grams of acrylic acid, and 1.0 gram AIBN were combined with 1200 ml of ethyl acetate, purged with nitrogen and reacted for 48 hours at 45°C. The resulting solution was precipitated into methanol and dried. The molecular weight as determined by GPC analysis of the polymer was 744,000 Daltons.

Examples 6-19

Adhesive-coated sheet materials prepared using the various adhesive compositions whose properties are described above were compounded from the following materials. All compositions were compounded in accordance with the "Coating Solution Preparation Procedure" found in the "Adhesive Drawdown Coating Procedure" above, with the exception of Example 14 which required heat during the compounding process. The transition temperatures reported in Table 3 are the recorded peak crystalline melt temperature of the crystalline component as is ("Pre-blend") and as admixed with the conventional adhesive ("Post-blend"). All melt points were determined using a differential scanning calorimeter. Gelva® 737 is a commercially available PSA manufactured by Monsanto Chemical Company. Morstik® 607 and Morstik® 103 are commercially available PSAs manufactured by Morton International. VYBAR® 103 is a commercially available polyethylene produced by Petrolite Speciality Polymer Group.

Table 3
Adhesive Coating Compositions, Properties and Solvents

<u>Adhesive</u>	<u>Conventional Adhesive (%)</u>	<u>Crystalline Component (%)</u>	<u>Additive (%)</u>	<u>Transition Temp. (°C) Pre-blend</u>	<u>Transition Temp. (°C) Post-blend</u>	<u>Solvent</u>
Example 6	Gelva® 737 (65)	Example 1 (35)		41.6	40.5	Toluene
Example 7	Morstik® 607 (65)	Example 1 (35)			40.0	Toluene
Example 8	Morstik® 103 (65)	Lanolin (35)			N/A	Hexane/Toluene/ Cyclohexane (64/23/13)
Example 9	Morstik® 103 (85)	Example 2 (15)		44.7	36	Hexane/Toluene/ Cyclohexane (76/12/12)
Example 10	Morstik® 103 (65)	Example 3 (22)	Lanolin (13)	45.1	38	Hexane/Toluene/ Cyclohexane (69/20/11)
Example 11	Morstik® 103 (75)	Eicosane (25)		37	33	Hexane/Toluene/ Cyclohexane (62/24/14)
Example 12	Morstik® 103 (75)	Example 5 (25)		48	39	Hexane/Toluene/ Cyclohexane (69/20/11)

Table 3. continued
Adhesive Coating Compositions, Properties and Solvents

<u>Adhesive</u>	<u>Conventional Adhesive (%)</u>	<u>Crystalline Component (%)</u>	<u>Additive (%)</u>	<u>Transition Temp. (°C) Pre-blend</u>	<u>Transition Temp. (°C) Post-blend</u>	<u>Solvent</u>
Example 13	Morstik® 103 (75)	Example 4 (25)		71	63	Hexane/Toluene/ Cyclohexane (55/31/14)
Example 14	Morstik® 103 (75)	VYBAR 103 (25)		71	62.6	Xylene
Example 15	Gelva® 737 (100)				N/A	Ethyl Acetate/ Ethanol/Toluene (48/40/12)
Example 16	Morstik® 607 (100)				N/A	Ethyl Acetate/ Isopropanol/ Pentadione
Example 17	Morstik® 103 (100)				N/A	Ethyl Acetate/ Cyclohexane (80/3/17)
Example 18	Morstik® 103 (87)	Lanolin (13)			N/A	Hexane/Toluene/ Cyclohexane (69/17/14)
Example 19	Morstik® 103 (65)	Example 5 (22)	Lanolin (13)	48	39	Hexane/Toluene/ Cyclohexane (69/20/11)

Examples 20-36

Table 4 below shows the peel adhesion values of adhesive compositions 4°C below and above the melting temperature of the incorporated crystalline component.

- 5 The unmodified adhesives do not undergo any phase changes within the desired evaluation range. Hence, their evaluation temperatures were dictated by the other adhesive compositions. The peel adhesion values were determined in accordance to the Standard Peel Test
- 10 Procedure designed for the specific adherent surface as listed above. The adhesive coatings were prepared in accordance to one of the Adhesives Drawdown Coating Procedures, noted above, except for Example 14 which required a heated coating surface and a higher drying
- 15 temperature (130°C). All coatings were made using the Direct Coating Method unless otherwise noted as (TCM). These coatings were done using the Transfer Coating Method (TCM). The transition temperature was determined by thermal analysis. All Examples were tacky at
- 20 temperatures below and above the NUTZ unless otherwise noted by (NT).

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Table 4
Peel Adhesion Values on Various Substrates

<u>Example</u>	<u>Adhesive Coating Example</u>	<u>Base Adhesive</u>	<u>Crystalline Component Type/Mw</u>	<u>Loading (% by Weight)</u>	<u>Adherent Surface</u>	<u>Peel Adhesion (grams/cm)</u>
						<u>Within NUTZ</u> <u>Above NUTZ</u>
20						
21						
22	15 (TCM)	Acrylic			Tuftane	96.3 103
23	6 (TCM)	Acrylic	SCCP/Low	35	Tuftane	72.5 (NT) 20.0
24	16 (TCM)	Acrylic			Tuftane	117 92.2
25	7 (TCM)	Acrylic	SCCP/Low	35	Tuftane	55 (NT) 12.7
26	17	Styrene butadiene rubber (SBR)			Stainless Steel (S. S.)	1398 1066
27	8	SBR	Lanolin	35	S. S.	410 248
28	9	SBR	SCCP/Low	15	S. S.	0 (NT) 598
29	10	SBR	SCCP/Low	22	S. S.	305 (NT) 10
30	11	SBR	MCCP/Low	25	S. S.	195 (NT) 10
31	12	SBR	SCCP/High	25	S. S.	Low (NT) 393
32	13	SBR	SCCP/Low	25	S. S.	Low (NT) High
33	14	SBR	MCCP/High	25	S. S.	Low (NT) High
34	18	SBR	Lanolin	15	Skin	61 54

Table 4, continued
Peel Adhesion Values on Various Substrates

<u>Example</u>	<u>Adhesive Coating Example</u>	<u>Base Adhesive</u>	<u>Crystalline Component Type/Mw</u>	<u>Loading (% by Weight)</u>	<u>Adherent Surface</u>	<u>Peel Adhesion (grams/cm)</u>	
						<u>Within NUTZ</u>	<u>Above NUTZ</u>
35	19	SBR	SCCP/High	22	Skin	29 (NT)	25
36	10	SBR	SCCP/Low	22	Skin	57 (NT)	7
37	6 (TCM)	Acrylic	SCCP/Low	15	Tuftane	67.4 (NT)	58
38	6 (TCM)	Acrylic	SCCP/Low	25	Tuftane	61.7 (NT)	16.1
39	6 (TCM)	Acrylic	SCCP/Low	55	Tuftane	<15 (NT)	<15

Example 40

This example shows the different behavioral temperature characteristics of this unique class of adhesive compositions. Figure 1 illustrates how temperature changes affect the adhesivity of TZS-PSA and other PSAs to a smooth nonporous backing such as stainless steel. The upper limit of NUTZ is positioned at 35°C by the above definition.

This particular TZS-PSA of Example 10 reacted markedly differently upon warming as compared with the other PSA adhesives. The neat SBR adhesive was tacky at all temperatures and, more or less, maintained its adhesive bond strength as the evaluation temperature was increased from 30° to 40°C. Similarly, the lanolin-enriched SBR adhesive was tacky at all temperatures and retained its initial peel adhesion properties over the same temperature range. In contrast, the TZS-PSA was tacky only above the lower limit of NUTZ and exhibited peel adhesion properties similar to that of the other PSA examples when the evaluation temperature was in the NUTZ, and then underwent an abrupt 20-fold drop in peel adhesion over a relatively narrow temperature increase of 4°C from 32° to 36°C and a 35-fold reduction in peel adhesion when raised from 32° to 38°C. As the temperature was increased above the upper limit of NUTZ, adhesivity was completely diminished without losing any cohesive strength.

Figure 2 compares the effect of temperature on the tack and peel adhesion of the TZS-PSA to a nonporous stainless steel substrate. The data indicate that the tack of the TZS-PSA begins suddenly at 32°C and increases thereafter as the temperature increases. Below the NUTZ, the TZS-PSA was substantially nontacky. However, as the evaluation temperature was raised, the tack dramatically

increased and the composition became aggressively tacky. For the composition shown above, the tack transition temperature (lower NUTZ limit) was approximately 32°C. Conversely, the peel adhesion of this TZS-PSA decreased with unexpected sharpness as the evaluation temperature was increased above the NUTZ. For the composition shown above, the peel strength adhesion transition temperature (upper NUTZ limit) was approximately 35°C. The tack and peel adhesion transition temperatures dictated the lower and upper temperature boundaries, respectively, for which the TZS-PSA possessed both tack and adhesivity. Hence, in 32°C-35°C temperature zone, the above TZS-PSA composition behaved similar to common pressure-sensitive adhesives.

Figure 2 also illustrates that good adhesive bonding can be achieved when the adhesive article is used below the NUTZ. For example, this TZS-PSA had no tack at 30°C. Yet if it was warmed above 32°C, it developed tack and stuck to the substrate. It also stuck well to the substrate when its temperature was reduced below the NUTZ as shown on the graph at 30°C. Thus, this TZS-PSA can exhibit the property of not sticking to a substrate initially at 30°C, but sticking to it between 32°C and 36°C, sticking to it when cooled back to 30°C, and then not sticking to it when the temperature is finally raised to 38°C.

Example 41

This example demonstrates how the prepositional and removable features of these unique adhesive compositions can be used. A sample of 1.5 mil adhesive film made according to Example 10 was produced on a silicon release liner. That assembly was placed behind a 3 x 5 photograph, the back of which had been lightly

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sanded, and put in a heated press that was preheated to 45°C. A pressure of 5000 psi was applied to the laminate for about 5 minutes. The laminate was removed from the press and allowed to cool to room temperature (19°C) under the weight of a five pound weight. The excess film material was trimmed from the photograph. The protective release liner was removed.

The photograph was now ready to mount. It was positioned on the page of a photo album. Because there was little or no appreciable tack, it was easy to move to a different position on the page. When its final location was determined, it was held down to the page on two of its corners while it was gently warmed by a conventional hair dryer. Immediately the back of the photograph became tacky and began to stick to the page as if it had been coated with a normal PSA. The photograph was secured to the page by lightly rubbing it with a clean cloth. It was reheated with the hair dryer for an additional 15 seconds and lightly rubbed again. After one minute it had cooled down to room temperature. An attempt to remove a corner of the photo resulted in tearing the photo album page below that corner. The following day an attempt to remove another corner of the photo was made. Similar damage was done. The photo album was placed in the refrigerator overnight and then allowed to warm up to room temperature the next morning. Another attempt to remove another corner of the photo was made but met the same consequence as above. Finally, the photo was reheated with the hair dryer and was easily removed without staining or damage to the page to which it had been attached without leaving adhesive residue.

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Example 42

This example demonstrates how the removable features of these unique adhesive compositions can be applied to a tamper-proof label. A sample of 1.5 mil adhesive film was made according to Example 10 but involved a modification of the crystalline polymer as described in Example 2 (except that the reaction mixture contained sufficient hexadecylacrylate to reduce the transition temperature of the final polymer to 29°C). The composition was cast on a silicon release liner. That assembly was then placed on a sheet of newspaper and put in a heated press that was preheated to 45°C. A pressure of 5000 psi was applied to the laminate for about 5 minutes. The laminate was removed from the press and allowed to cool to room temperature. Small strips measuring 1 x 2 cm were cut from the sheet. The release liners were removed from the strips and three of them were pressed on a glass jelly jar, a plastic pen, a stainless steel panel and a magazine. After one hour, an attempt to remove one or the strips from each object held at room temperature was made. In all cases, the paper was torn during the removal process. Next, the objects were placed in the refrigerator for one hour. Another attempt was made to remove the strips from them. All were successfully removed with the exception of the magazine strip. The last remaining strip on each of the objects was easily and successfully removed by heating with a hair dryer and left no residue on the substrate.

Example 43

Three of each of the strips used in example 36 were placed on a moderately hairy portion of the arm of three volunteers. The samples were worn for periods of 1, 6 and 24 hours, each subject wearing such for one of

the designated periods. One of the strips on each of the volunteers were at ambient temperature by pulling from one end of the strip at an angle that was perpendicular to the surface of the arm. Removal was accomplished at a rate of 1 inch/second. In all cases, pain was experienced and both cells of the stratum corneum and hair were found on the surface of the strips. The second strip on each volunteer was cooled with an ice cube for 10 seconds and then removed in the manner described above. Pain was reported and a similar amount of cellular debris and hair was found on the surface of the strips. The third strip on each volunteer was heated with a hair dryer as it was removed in the manner described above. No pain was reported and no cellular debris or hair was found on the surface of those strips.

Example 43 provides a valuable demonstration of the usefulness of the adhesive compositions of the present invention. By including such adhesive compositions on bandages, the bandage can be applied to the skin at room temperature at which temperature the bandage adhesive has sufficient tackiness to allow the bandage to adhere to the skin. The temperature of the adhesive is then raised to body temperature as it is worn. However, at the body temperature or wearing temperature, the adhesive binds to and adheres to the skin. This demonstrates the normal use temperature zone of the adhesive in that the temperature range at which the adhesive is tacky and can be applied is within normal room temperature ranges and the temperature at which the adhesive adheres to and binds the skin is within normal mammalian body temperatures (preferably about 32-34°C). Further, the adhesiveness of the bandage to the skin is maintained even though the adhesive composition is cooled

by ice. Even if the tackiness of the composition would be greatly deteriorated by such cooling, the composition continues to adhere to the porous skin surface. When the removal of the bandage is desired, it is heated to a range which is outside of the normal use temperature zone which, for this composition, is somewhat (10-20 centigrade degrees) above body temperature. At this point, the crystalline polymers within the adhesive composition pass their first order transition point and cause the composition to lose its ability to adhere to the skin. Accordingly, at such temperature, the bandage can be removed easily without subjecting the patient to pain.

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Example 44

The following formulation was made and warmed slightly until a clear solution was obtained: 60 parts X7-4201 (a silicone pressure-sensitive adhesive composition supplied by Dow Corning), 10 parts PS-135 (polymethylhexadecylsiloxane) (Hüls) having a melting point of 35°C and a molecular weight of 10,000, and 30 parts toluene. The solution was cast as a 1 mil thick film on a Mylar backing using a Meyer rod. The composite was dried in an oven at 90°C for 30 minutes. When tested against a stainless steel substrate, the peel strength was 300 g/cm at 30°C and 172 g/cm at 45°C, thus showing a peel strength reduction of 43%.

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Example 45

An acrylic resin was made by polymerizing 2-ethylhexyl acrylate ("2-EHA", 37.9 parts) and acrylic acid ("AA", 2 parts), using ethyl acetate ("EA", 59.9 parts) as the solvent and AIBN (0.2 parts) as the

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initiator. The materials were heated under nitrogen for 16 hours. The resulting polymer had a molecular weight average of 603,000 as determined by GPC.

A series of polymers, consisting of
5 octadecylacrylate, butyl acrylate and acrylic acid were polymerized by heating under nitrogen for 2.5 hours, using (Esperox 28 (t-butyl percotate, Witco Chemical)) as the initiator. The quantities used and the resultant polymer molecular weights are given below. The polymers
10 were precipitated in methanol and the molecular weight average determined by GPC.

The polymers prepared were each used as the crystalline polymer component in the following formulation.

15 2-EHA/AA polymer (42.86 parts), the selected crystalline polymer component (14.28 parts) and toluene (42.86 parts) were mixed. After mixing and warming to clarify them, the solutions were cast to give a 1 mil thick film on a backing of 1 mil thick Mylar. The
20 composite films were dried at 90°C for 30 minutes and tested on stainless steel at 30°C and 45°C.

The solubility parameter of both the resin and the crystalline components were calculated using group contributions according to Fedors (D.W. van Krevelen,
25 Properties of Polymers, published by Elsevier, second edition, p. 138).

The calculated solubility parameter of 2-EHA/AA 95/5 is 18.2 ($J^{1/2}/cm^{3/2}$): The solubility parameters of the crystalline polymer components were also calculated
30 and these values are included in Table 5.

Table 5
Polymer Compositions, Molecular Weight
Average and Melting Point as Determined by DSC

	A	B	C	D	E
C18A	85	80.8	78.6	76.5	72.25
C4A	13	14.2	13.9	13.5	12.78
AA	2.0	5.0	7.5	10.0	15.0
C12SH	5.0	5.0	5.0	5.0	5.0
Mw	8000	8696	9062	8973	8205
Tm2	40.2	40.4	43.3	43.3	42.6
Formulation	1	2	3	4	5
Peel strength 30°C g/cm	32	75	80	104	104
45°C g/cm	32	18	17	17.6	80.15
% reduction on warming	0	76	78.7	83	22.7
% acrylic acid	2	5	7.5	10	15
calculated solubility parameter	18.15	18.6	18.93	19.22	19.72

Table 6

Formulation	6	7	8	9	10
Peel strength 30°C	102.8	61.9	60.1	67.6	70
45°C	82	45.5	15.6	29.7	156CF
% reduction in peel strength	20.2	26.5	74	41	-122
% acrylic acid	2	5	7.5	10	15
calculated solubility parameter	18.15	18.6	18.93	19.22	19.72

CF indicates cohesive failure of the bond.
Potential areas to be claimed.

The moisture vapor transmission of the resultant film when formulation 4 was coated onto the Hytrel backing was measured by ASTM E96-90 and found to be $140 \text{ g/m}^2/24$ hours at 37°C and a relative humidity difference of 100% to 10%.

A second polymer was made having an increased moisture vapor transmission by polymerizing with ethoxy ethyl acrylate. The resulting polymer, 70/25/5 2-ethylhexyl acrylate/ethoxy ethyl acrylate/acrylic acid, had a molecular weight average of 741,000. The calculated solubility parameter is 18.41. A series of formulations were made using crystalline polymers, A, B, C, D and E in the same proportions given above, and these are listed in Table 6 as formulations 6, 7, 8, 9 and 10. 2EHA/EEA/AA (70/25/5) 42.86 parts, crystalline polymer -- C18A/C4A/AA 14.28 parts, toluene 42.86 parts.

The moisture vapor transmission of the backing together with the adhesive was found to be $360 \text{ g/m}^2/24$ hours at 37°C at a relative humidity difference of 100% to 10% for the formulation containing 10% acrylic acid.

In Tables 5 and 6, C12SH represents dodecyl mercaptan, C18A represents a C_{18} acrylate, and C4A represents a C_4 acrylate.

Example 46

The following formulation was prepared: crystalline polymer, 13 parts (a C_{18} acrylate/ C_4 acrylate copolymer having a ratio of 96/4, a molecular weight of 6 K, and a T_m of 45°C); 78 parts styrene-butadiene rubber (Morstik® 112); and 9 parts polybutene ("Polybutene H 100", obtained from Amoco). The peel strength of the formulation on stainless steel with a backing of 2.3 mil Mylar polyester was found to be 504 g/cm at 30°C and 49

g/cm at 40°C. When skin tested on a group of six people using a 1 inch strip of adhesive on the inside of the forearm, the peel strength was 53 g/cm at ambient temperature, reducing to 13 g/cm when warmed. The
 5 formulation was also found to give improved wear performance on skin in that it could be worn in a hot shower without showing lift off at the edges.

Example 47

10 This example illustrates the minimum amount of crystalline polymer needed in an acrylate based adhesive system.

The adhesive compositions were produced from a base adhesive of 2-ethylhexylacrylate and acrylic acid
 15 (95:5), with a molecular weight (Mw) of 694,000 Daltons. To the base adhesive, the crystalline polymer (C18 acrylate/C4 acrylate/acrylic acid, 78.6/13.9/7.5 Mw 9062 Daltons) was added at 0.5, 4, 14, and 25% based on weight of base polymer. The adhesive was coated onto 1 mil.
 20 Mylar to achieve a 1 mil. coating thickness (after drying 30 min @ 90°C.). The coated material was then peel tested (180°C, 12 in/min) on stainless steel at 30°C and 45°C. The results were as follows:

25	% Crystalline Polymer	Peel Strength		Reduction in Peel Strength (%)
		30°C	45°C	
	0.0	275	206	25
	0.5	138	58	57
	4.0	78	42	46
30	14.0	64	15	76
	25.0	60	15	75

The conclusion from these data is that in an acrylic system, it is possible to achieve a greater
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reduction in peel strength on warming than is achieved in a control, when using as little as 0.5% crystalline polymer.

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Example 48

This example ullustrates the minimum amount of crystalline polymer needed in a styrene-butadiene-rubber (SBR) based adhesive system.

10 The adhesive compositions for this example were produced from a commercial SBR adhesive (Morstik 112), crystalline polymer (C18A/C4A 96/4) and lanolin. A matrix of five polymers was produced, varying the amounts of crystalline polymer and lanolin. Each adhesive solution was coated onto Mylar to achieve a 1 mil film
15 after drying. The coated materials were then peel-tested (180° 12 in./min.) on stainless steel at 30°C and 42°C. The results are as follows:

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	Formulation	Peel Strength (g/cm)		Tack
		30°C	42°C	
5				
10				
15				
20				
25				
30				
35				
	1. 75/20/5	337	0	Poor
	2. 90/5/5	679	515	Excellent
	3. 75/12.5/12.5	299	0	Slight
	4. 60/20/20	178	0	Slight
	5. 75/5/20	315	84	Good

The conclusion from these data is that it is possible to achieve a reduction in peel strength, while maintaining good tack properties, on warming with as little as 5% crystalline polymer.

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The present adhesive compositions and articles which include such compositions have been shown and described herein in what is considered to be the most practical, and preferred embodiments. It is recognized, however, that departures may be made therefrom which are within the scope of the invention and that obvious modifications will occur to one of ordinary skill in the art upon reading this disclosure.

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Claims

1. A temperature zone specific pressure-sensitive adhesive (TZS-PSA) composition for affixing an
5 article to a substrate at a temperature within a normal use temperature zone (NUTZ) bounded by a minimum temperature and a maximum temperature, wherein the composition comprises:

- (a) approximately 50 wt.% to 99 wt.% of a
10 polymeric, pressure-sensitive adhesive component; and
(b) admixed intimately therewith, approximately
1 wt.% to 50 wt.% of a crystalline polymer that is partially miscible with the polymeric, pressure-sensitive adhesive component and has a heat of fusion of at least
15 about 20 Joules/g,

wherein the NUTZ encompasses the temperature range within which the TZS-PSA maintains at least some tackiness and retains both adhesive and cohesive strength when bonded to a substrate.

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2. The composition of claim 1, wherein the crystalline polymer has a molecular weight of between about 3,500 and 25,000 Daltons and is selected such that bond strength between the TZS-PSA and a substrate
25 decreases when the composition is warmed to above the maximum temperature.

3. The composition of claim 1, wherein the crystalline polymer is selected such that the TZS-PSA is
30 substantially nontacky at temperatures below the minimum temperature but becomes tacky and capable of bonding to a substrate when warmed to a temperature above the minimum temperature.

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4. The composition of claim 1, wherein the crystalline polymer has a molecular weight in the range of about 3,500 to 25,000 Daltons and is selected such that the TZS-PSA is substantially nontacky at
 5 temperatures below the minimum temperature, becomes tacky and capable of bonding to a substrate when warmed to above the minimum temperature, and loses bond strength when warmed to temperatures above the maximum temperature.

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5. The composition of claim 1, wherein the crystalline polymer is selected such that the bond strength between the TZS-PSA and a substrate to which it is affixed decreases when the composition is cooled to
 15 below the minimum temperature.

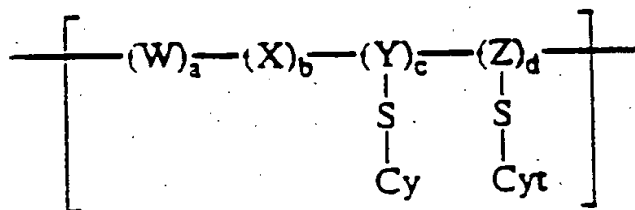
20

6. The composition of claim 5, wherein the crystalline polymer has a molecular weight in the range of about 100,000 to 900,000 Daltons.

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7. The composition of claim 1, wherein the crystalline polymer is a side-chain crystallizable polymer containing recurring units having the structural formula

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wherein W and X are each respectively a first and a second monomer unit, which monomer unit may be any

molecular moiety connectable to an adjoining molecular moiety, Y and Z are each independently a backbone monomer unit which may be any molecular moiety or atom, each S is independently a linking group or spacer unit and is
5 optionally present, Cyt and Cy are each independently a crystallizable moiety connected to the respective backbone, and a, b, c and d are each, independently, integers ranging from 0 to 1,000 with the proviso that
10 sufficient Cyt and Cy are present so as to provide a molecular weight which is equal to or greater than twice the sum of the molecular weights of W, X, Y and Z, and wherein the molecular weight of the polymer is less than about 900,000 Daltons.

15 8. The composition of claim 1, wherein the crystalline polymer is a main-chain crystallizable polymer.

20 9. The composition of claim 1, wherein the NUTZ is such that the TZS-PSA is compatible for use with human skin.

25 10. The composition of claim 1, comprising approximately 65 wt.% to 95 wt.% polymeric, pressure-sensitive adhesive component and 5 wt.% to 35 wt.% crystalline polymer.

30 11. An adhesive assembly which may be affixed to a substrate at a temperature within a normal use temperature zone (NUTZ) bounded by a minimum temperature and a maximum temperature, wherein the composition comprises:

35 (a) approximately 50 wt.% to 99 wt.% of a polymeric, pressure-sensitive adhesive component; and

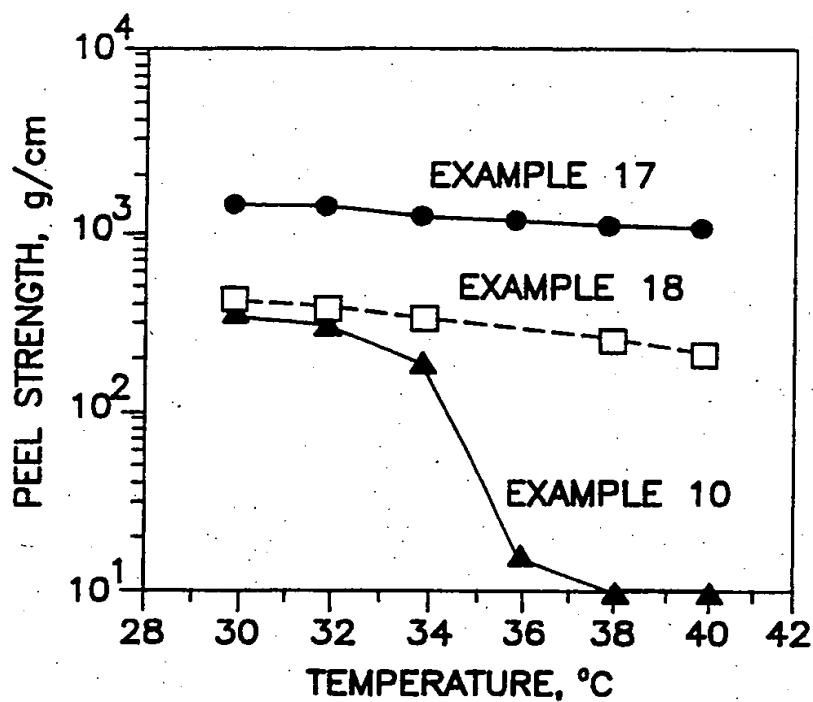
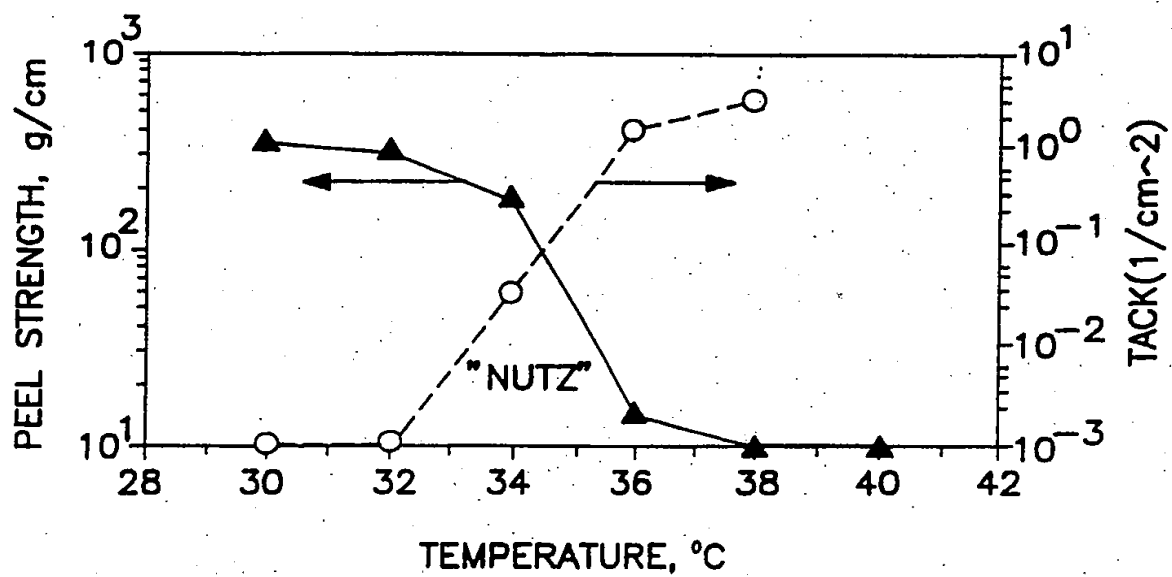
(b) admixed intimately therewith, approximately 1 wt.% to 50 wt.% of a crystalline polymer that is partially miscible with the polymeric, pressure-sensitive adhesive component and has a heat of fusion of at least about 20 Joules/g,

wherein the NUTZ encompasses the temperature range within which the TZS-PSA maintains at least some tackiness and retains both adhesive and cohesive strength when bonded to a substrate.

12. The adhesive assembly of claim 10, having a moisture vapor transmission rate of at least about 100 g/m²/day.

13. The adhesive assembly of claim 10, wherein the adhesive has a moisture vapor transmission rate of at least about 500 g/m²/day.

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**FIG. 1****FIG. 2**

INTERNATIONAL SEARCH REPORT

PCT/US92/01153

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)				
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C08F 8/00, 283/12; C08L 9/00, 27/12, 29/00, 31/00, 33/00, 33/04 U.S. CL. 525/92, 93, 94, 96, 98, 123, 187, 188, 191, 199, 217, 218, 227 (Cont.)				
II. FIELDS SEARCHED				
Minimum Documentation Searched *				
Classification System	Classification Symbols			
U.S.	525/92, 93, 94, 96, 98, 123, 187, 188, 191, 199, 217, 218, 227, 231, 404, 408, 455, 479			
Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched *				
III. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.		
X	US, A, 4,143,858 (SCHMIDT, III); 13 MARCH 1979 See entire document.	1-13		
X	US, A, 4,186,258 (SCHMIDT, III); 29 JANUARY 1980 See entire document.	1-13		
Y	US, A, 4,778,852 (FUTAMURA); 18 OCTOBER 1988 See columns 1-8.	1-13		
Y	US, A, 4,835,199 (FUTAMURA); 30 MAY 1989 See entire document.	1-13		
Y	US, A, 4,973,615 (FUTAMURA); 27 NOVEMBER 1990 See entire document.	1-13		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> * Special categories of cited documents: <ul style="list-style-type: none"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; vertical-align: top; border: none;"> <ul style="list-style-type: none"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family </td> </tr> </table>			* Special categories of cited documents: <ul style="list-style-type: none"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed 	<ul style="list-style-type: none"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family
* Special categories of cited documents: <ul style="list-style-type: none"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed 	<ul style="list-style-type: none"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family 			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report			
21 APRIL 1992	26 MAY 1992			
International Searching Authority	Shirley A. Wright			
ISA/US				

Continuation: I. CLASSIFICATION OF SUBJECT MATTER

IPC (5): C08L 33/06, 35/00, 39/00, 47/00, 53/00, 71/02, 75/00,
77/00, 85/02; C09J 123/00, 125/00, 125/04, 125/06,
125/14, 127/00, 127/06, 131/02, 133/00, 133/04,
133/10, 133/14
U.S. CL. 525/231, 404, 408, 455, 479

